

UNIVERSITY OF TECHNOLOGY SYDNEY

DOCTORAL THESIS

Optical Transport of Pseudo-Random Coatings

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Declaration of Authorship

I, Marc A. GALÍ LABARIAS, declare that this thesis titled, “Optical Transport of Pseudo-Random Coatings” and the work presented in it are my own. I confirm that:

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- Where I have consulted the published work of others, this is always clearly attributed.
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- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.
- This research is supported by an Australian Government Research Training Program.

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"All truths are easy to understand once they are discovered; the point is to discover them. "

Galileo Galilei

UNIVERSITY OF TECHNOLOGY SYDNEY

Abstract

Science

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Optical Transport of Pseudo-Random Coatings

by Marc A. GALÍ LABARIAS

Coatings are widely used to improve the optical performance of surfaces exposed in the built environment, technological devices, and consumer goods. In the last decades the improvement of techniques to create structured coatings has hugely increased the range of properties that can be achieved by such systems. Unfortunately, the theoretical techniques to model the complex and often pseudo-random nature of structured coatings are not yet fully adequate. In this thesis I will address this problem. Specifically, I will develop improved techniques that can be used on different kinds of coatings: mesoporous metals, random two-phase structures, heterogeneous matrices and rough surfaces.

First, I will consider silver mesoporous sponges. These are both random and isotropic, and are readily synthesized in the laboratory in various physical densities. Therefore they provide a useful platform on which to begin developing computational strategies. I will analyse these structures using an *effective medium approximation* based on their far-field response. Mesoporous metals offer a very distinct optical response compared to their constitutive bulk metal. In particular, the topology of such structures creates metal systems with low plasmon response but with high conductivity thanks to their percolated metal *filaments*. These characteristics make them suitable for many applications, for example as highly absorptive optical coatings.

Next, I will introduce the concept of anisotropy into the coating structure by analysing columnar morphologies obtained using physical vapour deposition. These kind of coatings offer some degree of order caused by shadowing effects, and a degree of randomness due to the statistical roughening present when depositing such structures. The most important structural dependence is the plane perpendicular to the growth direction, hence in this work I will analyse them as two-dimensional structures. I will obtain the effective permittivity and optimal bounds (which I will call *leaf bounds*) by expanding the averaged polarization field in a power series on the susceptibility. To

do this we developed a method that relies on a Monte Carlo algorithm to efficiently obtain higher orders of this series expansion. Therefore, this new methodology permits the study of higher order micro-structural parameters. In this thesis I will analyse up to fourth order effects. For anisotropic coatings, the depolarization of the Gaussian random fields studied is related to the depolarization factors of an ellipsoid with the same anisotropy. This fact will make it relatively easy to design simple anisotropic structures that are optically equivalent to experimentally measured ones. Coatings of this type are useful for angular, spectral or polarization selectivity.

Thirdly, having explored single-material structures that are either random isotropic (sponges) or pseudo-random anisotropic (columnar), I turn to the problem of heterogeneous systems. The prototypical example is a paint-like coating in which some phases are randomly distributed inside a light-absorbing matrix. I will present a *generalized four-flux method* which is capable of analysing the optical response of realistic heterogeneous matrices. My new methodology is capable of dealing with factors including different size distribution of components, heterogeneous mix of materials, and weak absorption by the matrix (binder). A matrix formalism is developed to extend this method to multi-layer systems. The methodology is applied to the optimization of paints for achieving solar efficiency and I find that multi-layer paints with larger particles in the outer layer offer better performance in the IR.

Finally, I use a variation of the *C-method* to examine the effect of surface roughness on optical properties. Surface roughness is present in any kind of coating, including any of those described above, and, depending on its scale size, the optical response can vary significantly as a function of angle and wavelength. I analyse the angular effects caused by changing the correlation length of a surface profile with a fixed groove depth, i.e. increasing the noise of the surface and the effective slope of the profile to determine the angular dispersion. The effect of roughness on the optical properties is exemplified by showing how it can control the perceived colour of a gold surface. I show that some tuning of optical properties is possible by this means. My findings include that a significant reduction on reflectance with short correlation length, and that angular colour dependence of rough gold profiles shows a blue-white colour for s-polarization and a yellow-reddish colour for p-polarization.

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Author's Contributions

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Contents

Declaration of Authorship	iii
Abstract	vii
Acknowledgements	ix
Author's Contributions	xi
1 Introduction	1
1.1 Introduction	1
1.2 Aims and Overview	3
2 Background Theory	7
2.1 Maxwell's Equations	7
2.2 Scattering	8
2.3 Polarization and Power Transport	10
2.4 Constitutive Relations and Intrinsic Anisotropic Optical Quantities . . .	12
2.5 Effective Medium Approximations	13
2.6 Monte Carlo Modelling	15
2.7 Concluding Remarks	16
3 Metal Sponges	17
3.1 Methodology	18
3.1.1 Simulation of Sponge Geometry	18
3.1.2 Discrete Dipole Approximation	19
3.1.3 Effective Medium Approach	20
3.2 Results	22
3.2.1 Optical Properties	22
3.2.2 Effective Media	24
3.3 Conclusion	26
4 Effective Permittivity of Random Two-Phase Anisotropic Composites	29
4.1 System Generation	31

4.1.1	Autocorrelation Functions	31
4.1.2	Level-Cut Gaussian Random Fields	33
	Orthant Probabilities	34
	Kernels	35
4.2	Anisotropic Random Structures	36
4.2.1	Column-like Structure Generation	41
4.3	Fundamental Electrostatic Theory of Composites	43
4.3.1	Implementation Outline	44
4.3.2	Geometry Specification	45
4.3.3	Iterative Series of the Polarization Field	46
4.3.4	Effective Permittivity Series Expansion: β Powers	48
4.3.5	Monte Carlo Based Method to obtain the \hat{A}_n Tensors	50
4.3.6	Effective Permittivity Series Expansion: Susceptibility Powers	53
4.4	Effective Permittivity Bounds and Padé Approximants	55
4.5	Optimal Leaf Bounds	59
4.5.1	Leaf Bounds Algorithm	61
4.5.2	Bounds Analysis	62
4.5.3	Extremal Structures	64
4.6	Micro-Structural Parameters	66
4.7	Discussion	67
4.7.1	Micro-Structural Parameters	68
	Isotropic Systems	68
	Anisotropic Systems	73
	Mixed Kernels	77
4.7.2	Macroscopic Permittivity	79
	Mixed Kernels	83
4.8	Conclusion	84
5	Heterogeneous Matrices	87
5.0.1	Classical Four-Flux Method	88
5.1	Generalized Four-Flux Method	91
5.1.1	Generalized Balance Equations	92
5.1.2	Reflectance and Transmittance Coefficients	93
5.1.3	Effective Volume Coefficients	95
5.1.4	Forward and Back Scattering Ratios	97
5.1.5	Size Distribution Function of Scatterers	100
5.1.6	Forward Average Path Length	101
5.1.7	Multilayer Formalism	101
5.2	Validating Results with Experimental Data	103

5.2.1	Sample preparation	104
5.2.2	Models of Experimental Data	105
5.3	Results and Discussion	107
5.3.1	Binder Absorption	108
5.3.2	Distribution of Sizes	109
5.3.3	Analysis of a Two-Layer Stack	115
5.4	Conclusion	116
6	Rough Surfaces	117
6.1	C-Method	120
6.1.1	Field Expansion	121
6.1.2	Boundary and Initial Conditions	126
6.1.3	Diffracted Field	127
6.1.4	Energy Conservation	131
6.2	Minimizing Propagation of Uncertainty	134
6.3	Generating Random Surface Profiles	137
6.4	Discussion of the Optical Response of Random Rough Surfaces	139
6.4.1	Method Validation	140
6.4.2	Randomness Effects on the Optical Response	141
6.4.3	Effective Slope to Determine Angular Dispersion	145
6.4.4	The Colour of Rough Gold	148
6.5	Conclusion	153
6.6	Addendum: Equivalent Metamaterial Interface	154
6.6.1	Space Transformation	154
6.6.2	Metamaterial Permittivity and Permeability	156
7	Summary	159
7.1	Future Work	160
A	Pseudo-Depolarization Factors	163
A.1	Curvature to depolarization approximation	163
A.1.1	Pseudo-depolarization Factors of an Ellipsoid	168
	Gaussian and Mean Curvatures	169
A.1.2	Relative Extreme Curvatures: Field Enhancement	171
A.1.3	Pseudo-depolarization Factors of an Hyperboloid	174
A.1.4	Pseudo-depolarization Factors of an Arbitrary Quadratic Coordinate Equation	176
A.2	Summary	177

B	Supplementary Material	179
B.1	Four-Flux coefficients	179
B.2	Metric Space	180
	Bibliography	181

List of Figures

1.1	Diagram showing the polarization delay produced by the effective response of a column-like structure.	4
1.2	Diagram of light interaction events on a paint system with flat interfaces.	5
1.3	Diagram of the light interactions on a cylindrical (1D grating) rough surface.	6
2.1	Picture showing the propagation of a plane wave. It can be seen the spatial relationship between the electric field, magnetic field and propagation vector.	10
2.2	This picture shows the orientation of the electromagnetic field for s-polarized light (left) and p-polarized light (right).	11
3.1	Simulated metallic ball sponges classified by initial aluminium content and number of sweeps. These simulations were generated by Michael Cortie.	22
3.2	Normalized efficiencies (cross section equals to $\pi 30^2 nm^2$) at 0 sweeps for sponges with an initial Al fill factor of 60% (left) and 85% (right).	23
3.3	Extinction efficiency of a spherical sponge at 0 sweeps in terms of the initial concentration of aluminium in the precursor alloy. To a first order approximation the latter quantity can be taken as the void fraction.	23
3.4	Comparison between the real part of the refractive index (left) and the extinction coefficient (right) of the effective medium of a sponge at 0 sweeps, and the refractive index of bulk silver (Johnson and Christy, 1972).	25
3.5	Real (left) and imaginary (right) parts of the effective permittivity of a ball sponge at 0 sweeps and at different concentrations of silver.	26
4.1	Top view of a silicon column-like structure, the Si was deposited by serial bideposition at oblique incidence. This structure was deposited by Matthew Arnold and the SEM picture was taken by Ed Walsby and edited by Matthew Tai.	30

4.2	On the left, we can see a heat-map in gray scale of the SEM image of the column-like structure shown in figure 4.1. Right picture shows the autocorrelation function of the left image, the white lines are the scaled cross-sections of the autocorrelation function.	32
4.3	In this figure we can see the unit cell, kernel and autocorrelation functions for systems generated with an exponential kernel. The fill factors analysed represent 10%, 50% and 90% of occupancy and anisotropy ratios defined as the ratio of the edges of the unit cell, hence $e_y/e_x = 1$ is the isotropic case.	38
4.4	In this figure we can see the unit cell, kernel and autocorrelation functions for systems generated with a Gaussian kernel. The fill factors analysed represent 10%, 50% and 90% of occupancy and anisotropy ratios defined as the ratio of the edges of the unit cell, hence $e_y/e_x = 1$ is the isotropic case.	39
4.5	In this figure we can see the unit cell, kernel and autocorrelation functions for systems generated with a sinc kernel. The fill factors analysed represent 10%, 50% and 90% of occupancy and anisotropy ratios defined as the ratio of the edges of the unit cell, hence $e_y/e_x = 1$ is the isotropic case.	40
4.6	Autocorrelation cross-sections in the horizontal direction (left) and vertical direction (right) of the SEM image (fig. 4.2) compared with structures generated using different kernels. These autocorrelations are the result of an ensemble average of 100 realizations.	41
4.7	From right to left: Unit cell of a structure generated with the mixed kernel defined in equation 4.11, mixed kernel used, the autocorrelation function of the unit cell and the cross-sections of each autocorrelation function.	43
4.8	In this figure several known bounds in the literature can be seen (<i>C.T.</i> stands for Cherkaev and Tartar, <i>H.S.</i> for Hashin and Shtrikman, <i>M.T.</i> for Milton and Torquato). These bounds have been obtained for a two-phase 2D material described by a square unit cell with a circle, where the occupancy phase has $\epsilon_1 = 10$ and fill factor of 80%, and the background phase has $\epsilon_2 = 1$ and fill factor of 20%.	62

- 4.9 This leaf bounds plot shows the effect of increasing the fill factor in a two-phase system with $\epsilon_1 = 10$ and $\epsilon_2 = 1$. Left hand side picture shows three different fill factors of a sphere in a square unit cell, with fill factors of 30%, 60% and 90% moving from the left corner to the right corner of the big leaf (0th order bounds) respectively. The right hand side picture is a zoom of the left corner of the leaf bound with 30% fill factor. 63
- 4.10 This figure show the relation between second order bounds and anisotropy for three different structures with fixed fill factor of 77%. In this figure, next to each leaf bound there is the unit cell that characterise each system (semi-axis ratio of the ellipses is 1.2). 64
- 4.11 Diagram showing which kind of plate-like structures achieve the edge of the second order bounds. 65
- 4.12 Study of isotropic systems generated with exponential kernels. On the left picture it is shown how the micro-structural parameter of third order ($\hat{\Upsilon}_3$) depends on the fill factor. On the right, it is shown the difference between the diagonal elements of the micro-structural parameter of fourth order ($\hat{\Upsilon}_4$) and its dependence on the fill factor. These results have been obtained averaging over 500 realizations. 70
- 4.13 Study of isotropic systems generated with Gaussian kernels. On the left picture it is shown how the micro-structural parameter of third order ($\hat{\Upsilon}_3$) depends on the fill factor. On the right, it is shown the difference between the diagonal elements of the micro-structural parameter of fourth order ($\hat{\Upsilon}_4$) and its dependence on the fill factor. These results have been obtained averaging over 500 realizations. 71
- 4.14 Study of isotropic systems generated with sinc kernels. On the left picture it is shown how the micro-structural parameter of third order ($\hat{\Upsilon}_3$) depends on the fill factor. On the right, it is shown the difference between the diagonal elements of the micro-structural parameter of fourth order ($\hat{\Upsilon}_4$) and its dependence on the fill factor. These results have been obtained averaging over 500 realizations. 72

- 4.15 Study of anisotropic systems generated with exponential kernels. On the left picture the anisotropy dependence of the difference of the diagonal elements of the micro-structural parameter of second order ($\Delta\hat{\Upsilon}_2$) and the depolarization factors of an ellipsoid with same degree of anisotropy (red line with dots) are shown. On the right, we show the difference between the diagonal elements of the micro-structural parameter of fourth order ($\Delta\hat{\Upsilon}_4$) in terms of the anisotropy ratio; we put an inset image with the leaf bounds up to fourth order of a solution at certain anisotropy (marked by the red circle with a cross). These results have been obtained averaging over 500 realizations. 74
- 4.16 Study of anisotropic systems generated with Gaussian kernels. On the left picture we show the anisotropy dependence of the difference of the diagonal elements of the micro-structural parameter of second order ($\Delta\hat{\Upsilon}_2$) and the depolarization factors of an ellipsoid with same degree of anisotropy (red line with dots). On the right, the difference between the diagonal elements of the micro-structural parameter of fourth order ($\Delta\hat{\Upsilon}_4$) in terms of the anisotropy ratio is shown; we put an inset image with the leaf bounds up to fourth order of a solution at certain anisotropy (marked by the red circle with a cross). These results have been obtained averaging over 500 realizations. 75
- 4.17 Study of anisotropic systems generated with sinc kernels. On the left picture we show the anisotropy dependence of the difference of the diagonal elements of the micro-structural parameter of second order ($\Delta\hat{\Upsilon}_2$) and the depolarization factors of an ellipsoid with same degree of anisotropy (red line with dots). On the right, the difference between the diagonal elements of the micro-structural parameter of fourth order ($\Delta\hat{\Upsilon}_4$) in terms of the anisotropy ratio is shown; we put an inset image with the leaf bounds up to fourth order of a solution at certain anisotropy (marked by the red circle with a cross). These results have been obtained averaging over 500 realizations. 76
- 4.18 Third order (left) and fourth order (right) micro-structural parameters of mixed kernel structures at different volume fill factors. Different unit cells that represent these structures for different fill factor values on the bottom of the figure. These results have been obtained averaging over 500 realizations. 78

- 4.19 Simulated anisotropic parameters of a mixed kernel with the anisotropy in the sinc term. In the left plot we show the MSP of second order (black lines) and we compared it to the depolarization factors of an ellipsoid with same anisotropy ratios (red lines with dots). In the right image we show the MSP of fourth order and its dependence to the anisotropy, we put an inset plot to analyse the degree of anisotropy. Leaf bounds up to fourth order of a solution at certain anisotropy (marked by the red circle with a cross) are also shown. These results have been obtained averaging over 500 realizations. 79
- 4.20 Comparison between the macroscopic permittivity anisotropy of structures generated with different kernels (sinc results are possibly inaccurate due to insufficient sampling). 80
- 4.21 (Left) Difference between the diagonal terms of the effective permittivity depending on the fill factor bounded by the difference on the *leaf bounds*, $\lfloor \epsilon \rfloor - \lceil \epsilon \rceil$ and $\lceil \epsilon \rceil - \lfloor \epsilon \rfloor$. (Right) Numerical macroscopic permittivity values and their first and third order leaf bounds. Red represents first order leaf bounds, blue lines are third orders, and in black * the numerical solutions for each value, (left) $\hat{\epsilon}_y - \hat{\epsilon}_x$, and (right) $(\hat{\epsilon}_x, \hat{\epsilon}_y)$ 81
- 4.22 (Left) Difference between the diagonal terms of the effective permittivity depending on the anisotropy ratio at 50 % fill factor bounded by the difference on the *leaf bounds*, $\lfloor \epsilon \rfloor - \lceil \epsilon \rceil$ and $\lceil \epsilon \rceil - \lfloor \epsilon \rfloor$. (Right) Numerical macroscopic permittivity values and their first till fourth order leaf bounds. Red represents top leaf bounds $\lceil \epsilon \rceil$, while blue lines represents bottom leaf bounds $\lfloor \epsilon \rfloor$; and in black * the numerical solutions for each value, (left) $\hat{\epsilon}_y - \hat{\epsilon}_x$, and (right) $(\hat{\epsilon}_x, \hat{\epsilon}_y)$ 82
- 4.23 (Left) Difference between the diagonal terms of the effective permittivity depending on the fill factor bounded by the difference on the *leaf bounds*, $\lfloor \epsilon \rfloor - \lceil \epsilon \rceil$ and $\lceil \epsilon \rceil - \lfloor \epsilon \rfloor$. (Right) Numerical macroscopic permittivity values and their first and third order leaf bounds. Red represents first order leaf bounds, blue lines are third orders, and in black * the numerical solutions for each value, (left) $\hat{\epsilon}_y - \hat{\epsilon}_x$, and (right) $(\hat{\epsilon}_x, \hat{\epsilon}_y)$ 83
- 4.24 (Left) Difference between the diagonal terms of the effective permittivity depending on the anisotropy ratio at 50 % fill factor bounded by the difference on the *leaf bounds*, $\lfloor \epsilon \rfloor - \lceil \epsilon \rceil$ and $\lceil \epsilon \rceil - \lfloor \epsilon \rfloor$. (Right) Numerical macroscopic permittivity values and their first till fourth order leaf bounds. Red represents top leaf bounds $\lceil \epsilon \rceil$, while blue lines represents bottom leaf bounds $\lfloor \epsilon \rfloor$; and in black * the numerical solutions for each value, (left) $\hat{\epsilon}_y - \hat{\epsilon}_x$, and (right) $(\hat{\epsilon}_x, \hat{\epsilon}_y)$ 84

5.1	Diagram of the four-fluxes and interface parameters used in the four-flux model. $J_{c,d}$, $I_{c,d}$ are the incident collimated and diffused fluxes at each side of the slab; Z is the slab thickness; r_i^j are the reflection coefficients at the interfaces; superscript 0 refers to the side where J fluxes enter the slab, while Z refers to the side where I fluxes are incident; subscript d refers to diffused light, c for collimated; while subscript i refers to the interior edge and e to the exterior edge.	89
5.2	Angular scattering profile of a TiO_2 sphere of radius 80nm in acrylic: (Left) incident wavelength of 200nm; (Right) incident wavelength of 2000nm.	98
5.3	Angular scattering profile of a TiO_2 sphere of radius 1 μm in acrylic with incident wavelength of 2.5 μm	98
5.4	Diagram of the multilayer structure and notation.	102
5.5	SEM picture taken by Matthew C. Tai of a paint sample made of TiO_2 in acrylic binder.	105
5.6	Comparison between the reflectance of experimental and simulated data of an acrylic paint with 6% TiO_2 scatterers where their size follows a normal distribution with mean radius $\mu_0 = 90$ nm and standard deviation $\sigma = 18$ nm, and a 1% TiO_2 with a size distribution characterized by a mean radius $\mu_0 = 500$ nm and standard deviation of $\sigma = 100$ nm.	106
5.7	Comparison between the reflectance of experimental and simulated data of an acrylic paint with 14% TiO_2 scatterers where their size follows a normal distribution with mean radius $\mu_0 = 80$ nm and standard deviation $\sigma = 16$ nm.	107
5.8	Simulations of the spectra of acrylic paint with a normal distribution of TiO_2 particles of mean radius 0.08 μm and fill factor 10%; (left) without binder absorption; and (right) with absorption of the actual acrylic resin used included.	108
5.9	On the left side it can be seen a non-absorbing acrylic paint with a normal distribution of TiO_2 particles of mean radius 1 μm and fill factor 10%. Right graph shows acrylic paint with a normal distribution of TiO_2 particles of mean radius 1 μm and fill factor 10%.	109
5.10	These images show the optical response ((top-left) reflectance, (top-right) absorptance and (bottom) transmittance) of an acrylic matrix with TiO_2 sphere particles depending on the radius of those and on the incident wavelength.	110

- 5.11 (Top-left) Reflectance of acrylic paint for different size particle distributions. (Top-right) Gaussian distribution of particle radius for each paint. (Bottom-left) Back-scattering ratio of each distribution. (Bottom-right) Total scattering of each distribution. 112
- 5.12 Shows the effect of varying the standard deviation of the composite size distribution. This system represents an acrylic based paint with 14% of TiO_2 particles with fixed mean radius of $1.8 \mu\text{m}$ 113
- 5.13 Top-left figure shows the reflectance of 3 different paints. Top-right graph shows the size distribution of each paint. Bottom-left shows the backscattering ratio of each paint. Bottom-right shows the total scattering of each composition. 113
- 5.14 (a) Left image is a cartoon of the system modelled in the right image. The system is a two-layered stack with acrylic matrix and 7% of TiO_2 scatterers for both layers; first layer, particles with mean radius $1 \mu\text{m}$ and standard distribution 200 nm; second layer, particles with mean radius 100 nm and standard distribution of 20 nm. Reflectance, transmittance and absorptance are calculated for incidence fluxes from the left. (b) Left image is a cartoon of the system modelled in the right image. The system is a two-layered stack with acrylic matrix and a 7% of TiO_2 scatterers for both layers; first layer, particles with mean radius 100 nm and standard distribution of 20 nm; second layer, particles with mean radius $1 \mu\text{m}$ and standard distribution 200 nm. 115
- 6.1 This diagram presents the scenario under study, which gives a qualitative idea of the main variables of the problem: grooves depth h , period d , electromagnetic fields \vec{F} , \vec{G} , wave vector \vec{k} , incident angle θ , and permittivities of the different layers ϵ_i 121
- 6.2 These colormaps show the parallel components of the electromagnetic field interacting with a sinusoidal profile made of glass ($n=1.5$), this response is the result of an incident s-polarized plane wave (electric field parallel to the plane of incidence) propagating at normal angle to the material surface. 128
- 6.3 These colormaps show the parallel components of the electromagnetic field interacting with a sinusoidal profile made of glass ($n=1.5$), this response is the result of an incident p-polarized plane wave (magnetic field parallel to the plane of incidence) propagating at normal angle to the material surface. 129

- 6.4 These colormaps show the parallel components of the electromagnetic field interacting with a random generated profile made of glass ($n=1.5$), this response is the result of an incident s-polarized plane wave (electric field parallel to the plane of incidence) propagating at normal angle to the material surface. 130
- 6.5 These colormaps show the parallel components of the electromagnetic field interacting with a random generated profile made of glass ($n=1.5$), this response is the result of an incident p-polarized plane wave (magnetic field parallel to the plane of incidence) propagating at normal angle to the material surface. 131
- 6.6 Diagram of the regions of integration using Poynting Theorem. Note that the volume of integration is in the new coordinate system (x, u, z) , where the interface is flat. 132
- 6.7 Logical diagram of the algorithm used to attain the required number of modes for a good accuracy. The parameter δ is the breaking point for symmetric and smooth profiles (e.g $\sin(x)$), in our code is set to be -8 . This is needed because in these profiles the convergence of δ_{pm} is faster than δ_{cc} and thus, the optimization of N_0 is not needed. 136
- 6.8 These images show the evolution of δ_{pm} and δ_{cc} in terms of the number of modes. (left column) Comparison of the logarithm accuracies; (centre column) comparison of the accuracies values; (right column) profile under which the comparisons have been made. These calculations were made assuming an aluminium material illuminated under normal incidence with a wavelength of $10\mu m$; the grooves have an averaged height of $2.3\mu m$ and the grating has a period of $20.1\mu m$ 137
- 6.9 Four different random profiles using different correlation lengths. l_c is expressed as a fraction of a fixed RMS height h 139
- 6.10 Replication of figure (2) in the work presented by J. Chandezon, Dupuis, et al. (1982). The parameters used are: groove depth $0.12\mu m$, period of $1/3\mu m$ under Littrow configuration. G_0 profile is uncoated Aluminium (Rakić, 1995), on the other hand $G_1 - G_4$ have respectively 1 – 4 coatings of MgF_2 ($0.106\mu m$) and TiO_2 ($0.0602\mu m$). 140
- 6.11 Replication of figure (3-4) in the work presented by J. Chandezon, Dupuis, et al. (1982). These plots show the total reflectance and -1 order refracted energy depending on the ratio groove depth/period (h/d) for an Aluminium profile. Left picture shows the results for s-polarization (TE) while on the right pictures the profile is illuminated under p-polarized light (TM). The parameters used are: period $0.737\mu m$, groove depth over period (h/d) from 0 to 2.8, and incident angle of 23.6° 141

- 6.12 Average total reflectance for s-polarization and p-polarization at normal incidence depending on the incoming wavelength and the level of randomness h/l_c , where h is the average RMS height and l_c the correlation length. These are Aluminium (Rakić, 1995) profiles with an average RMS of $1.2 \mu\text{m}$ and super-period of $2 \mu\text{m}$, and results were averaged over 10 realizations. 142
- 6.13 Angular analysis of the averaged total reflectance of rough profiles increasing the level of randomness h/l_c , where h is the average RMS height and l_c the correlation length. Top row images show the total reflectance of Al (Rakić, 1995) profiles with average RMS of $1.2 \mu\text{m}$ and bottom row images profiles with average RMS of $2.3 \mu\text{m}$. In both cases the profiles studied have a super-period of $20 \mu\text{m}$ and the results were averaged over 10 realizations; the profiles were illuminated with a $10 \mu\text{m}$ wavelength. 143
- 6.14 Comparison of the angular-randomness dependence between: (left) Aluminium (Rakić, 1995) profiles and (right) Gold (Olmon et al., 2012) profiles. The optical response is shown through the percentage polarization reflectance ratio ($R_p/R_s \times 100$) between identical statistical profiles. The level of randomness is parametrised by h/l_c , where h is the average RMS height and l_c the correlation length. These profiles have an average RMS height of $2.3 \mu\text{m}$, period of $20 \mu\text{m}$ and incident wavelength of $10 \mu\text{m}$, and the results have been obtained over an average of 10 realizations. 144
- 6.15 BRDF of a Gold sine profile with height $2 \mu\text{m}$, period of $20.6 \mu\text{m}$ under an incident wavelength of $4 \mu\text{m}$. Left image shows the BRDF under p-polarization and in the right plot the profile is under s-polarization. Red crosses show the effective bounding angles and white dots shows the line of specular reflectance. 146
- 6.16 BRDF of a Gold sine profile with height $2 \mu\text{m}$, period of $30.7 \mu\text{m}$ under an incident wavelength of $4 \mu\text{m}$. Left image shows the BRDF under p-polarization and in the right plot the profile is under s-polarization. Red crosses show the effective bounding angles and white dots shows the line of specular reflectance. 146
- 6.17 BRDF of a Gold sawtooth profile with height $2 \mu\text{m}$, period of $6.6 \mu\text{m}$ under an incident wavelength of $4 \mu\text{m}$. Left image shows the BRDF under p-polarization and in the right plot the profile is under s-polarization. Red crosses show the effective bounding angles and white dots shows the line of specular reflectance. 147

- 6.18 BRDF of a Gold sawtooth profile with height $2\ \mu\text{m}$, period of $9.8\ \mu\text{m}$ under an incident wavelength of $4\ \mu\text{m}$. Left image shows the BRDF under p-polarization and in the right plot the profile is under s-polarization. Red crosses show the effective bounding angles and white dots shows the line of specular reflectance. 147
- 6.19 This figure shows the colour BRDF without specular reflectance of a gold surface with small roughness (RMS = 30 nm, correlation length = 50 nm and period $2\ \mu\text{m}$), and the BRDF for the different wavelength regimes associated to each colour: blue 450 - 490 nm; green 520 - 560 nm; and red 635 - 700 nm. In the first row we show the response for incident p-polarized light and second row shows the results under s-polarized light. These results have been obtain after averaging over 100 realizations. 150
- 6.20 Colour of shallow gold profiles caused only by scattering. The profiles of each row have different correlation lengths: top row $l_c = 20\ \text{nm}$, middle row $l_c = 200\ \text{nm}$, and bottom row $l_c = 2000\ \text{nm}$ 151
- 6.21 Colour of shallow aluminium profiles caused only by scattering. The profiles of each row have different correlation lengths: top row $l_c = 20\ \text{nm}$, middle row $l_c = 200\ \text{nm}$, and bottom row $l_c = 2000\ \text{nm}$ 152
- 6.22 Green line represents the surface profile; (left) solid lines are parallel to the canonical basis vector (\vec{e}_x) of the original coordinate system, (right) solid lines are parallel to the canonical basis vector (\vec{e}_v) of the transformed coordinate system. 155
- 6.23 Green line represents random surface profile; (left) solid lines are parallel to the canonical basis vector (\vec{e}_x) of the original coordinate system, (right) solid lines are parallel to the canonical basis vector (\vec{e}_v) of the transformed coordinate system. 156
- A.1 Relative error between *depolarization* and *pseudo-depolarization factors* depending on the ratio between the semi-axis, up to double the length. . . 165
- A.2 Relative error between *depolarization* and *pseudo-depolarization factors* depending on the ratio between the semi-axis, semi-axis ratio up to 10 times larger. 166
- A.3 This colormap represents the dependence of the *pseudo-depolarization factors* on the Gaussian curvature at the extreme point of $\theta = 0$ 171
- A.4 This plot represents function A.35 and A.36, i.e. it shows the real relative permittivity (ϵ'_r) in terms of the curvature parameter (C) in order to obtain resonance for an oblate ellipsoid for the two distinct semi-axis. . . 174

A.5	This colormap show the dependence of the <i>pseudo-depol. factors</i> on the principal curvatures.	176
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List of Abbreviations

EMF	E lectro M agnetic F ield
EMA	E ffective M edium A pproximations
UV	U ltra V iolet
VIS	V ISible
IR	I nfra R ed
NIR	N ear- I nfra R ed
MSP	M icro- S tructural P arameters
GRF	G aussian R andom F ield
LCGRF	L evel- C ut G aussian R andom F ield
BRDF	B idirectional R eflectance D istribution F unction

List of Symbols

\vec{E}	electric field	V m^{-1}
\vec{D}	electric displacement field	C m^{-2}
\vec{B}	magnetic inductance field	T
\vec{H}	magnetic field	A m^{-1}
\vec{P}	polarization field	C m^{-2}
\vec{F}	electric cavity field	V m^{-1}
$\hat{\epsilon}$	permittivity tensor	F m^{-1}
$\hat{\mu}$	permeability tensor	H m^{-1}
$\hat{\alpha}$	polarizability tensor	$\text{C m}^2 \text{V}^{-1}$
χ	susceptibility	
$m = n + ik$	complex refractive index	
ω	angular frequency	rad s^{-1}
c	speed of light	m s^{-1}
λ	wavelength	m
Q_{ext}	extinction efficiency	
Q_{sca}	scattering efficiency	
Q_{abs}	absorption efficiency	
Q_{pha}	phase efficiency	
C_{ext}	extinction cross-section	m^2
C_{sca}	scattering cross-section	m^2
C_{abs}	absorption cross-section	m^2
C_{pha}	phase cross-section	m^2
\hat{g}	metric tensor	
η	number density	m^{-3}
σ	standard deviation	

Chapter 3:

k	wavenumber	m^{-1}
x	scale parameter	
a	effective radius	m

Chapter 4:

p_n	n-point probability function	
$K(\vec{r})$	kernel function	
β_{ji}	polarizability	$\text{C m}^2 \text{V}^{-1}$
ϕ	fill-factor	
d	system dimension	
k	wavenumber	m^{-1}
$\mathcal{I}_i(\vec{r})$	indicator or occupancy function	
\mathbb{G}	Dyadic Green Tensor	
$\tilde{\mathbb{G}}$	Reduced Dyadic Green Tensor	
\hat{a}_n	system geometry tensor (permittivity series expansion)	
$\hat{\alpha}_n$	system geometry tensor (inverse permittivity series expansion)	
\hat{A}_n	Torquato's system geometry tensor (polarizability series expansion)	
\mathbb{A}_n	Monte Carlo system geometry tensor (polarizability series expansion)	
$\lfloor \cdot \rfloor_n$	n^{th} order lower bounds	
$\lceil \cdot \rceil_n$	n^{th} order upper bounds	
Υ_i	micro-structural parameters	

Chapter 5:

$n = n_1 + in_2$	complex refractive index	
k	absorption coefficient per unit length	m^{-1}
s	scattering coefficient per unit length	m^{-1}
ϵ	forward average path length	
β	backscattering ratio	
ζ	forward-scattering ratio	
K	total absorption coefficient per unit length	m^{-1}
S	total scattering coefficient per unit length	m^{-1}
$\tilde{\beta}$	average backscattering ratio	
$\tilde{\zeta}$	average forward-scattering ratio	
r	reflection coefficients	
R	total reflectance	
T	total transmittance	
ϕ	multi-layer transfer matrix	

μ_0	mean radius	m
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Chapter 6:

\vec{F}	field parallel to the surface	$\text{V m}^{-1} (\text{A m}^{-1})$
\vec{G}	field parallel to the incidence plane	$\text{A m}^{-1} (\text{V m}^{-1})$
k	wavenumber	m^{-1}
\vec{S}	Poynting vector	W m^{-2}
ε	efficiency	
α_n	horizontal component of the wavenumber	m^{-1}
β_n	vertical component of the wavenumber	m^{-1}
K	grating number	
d	super-period	m
l_c	correlation length	m

To my family

